Microplastics Analysis in the Environment

Making it fast, simple, easy & efficient

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Trusted Answers

Agilent at NEMC

Leveraging Instrument Sensitivity – Customers, Laboratories, and Regulators Benefitting from Evolving Lab Practices
Brian Pike, Lead Chemist, IDEA Lab
PACE Analytical

Virtual Lunch Seminar on Monday, August 17th will cover how the environmental testing industry offerings have been changing over time as a direct correlation to the sensitivity gains being realized through instrumentation for PFAS, Dioxins, sVOCs etc.

https://www.agilent.com/en/product/liquid-chromatography-mass-spectrometry-lc-ms

We Don't Yet Know the Potential Health Impacts for Humans

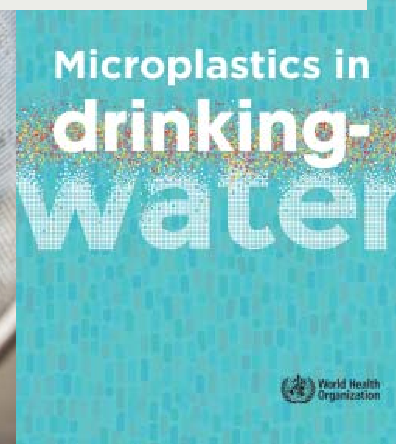
Global Health Organizations have Called for Additional Research

Given the potential impact, it is not surprising that global health organizations are also publishing reports on the impact of microplastics.

For example, in 2019, the World Health Organization (WHO) published a report, which concluded that there was not enough scientific evidence regarding the impact of microplastics on human health and more scientific research is required.

"The lack of standard methods for sampling and analyzing microplastics in the environment means that comparisons across studies are difficult... To better assess human health risks and inform management actions, a number of research gaps need to be filled."

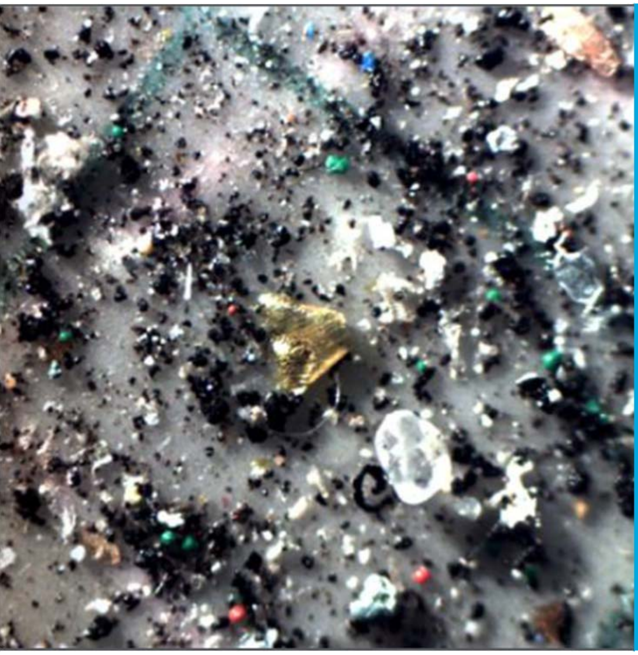
The World Health Organization, 2019.

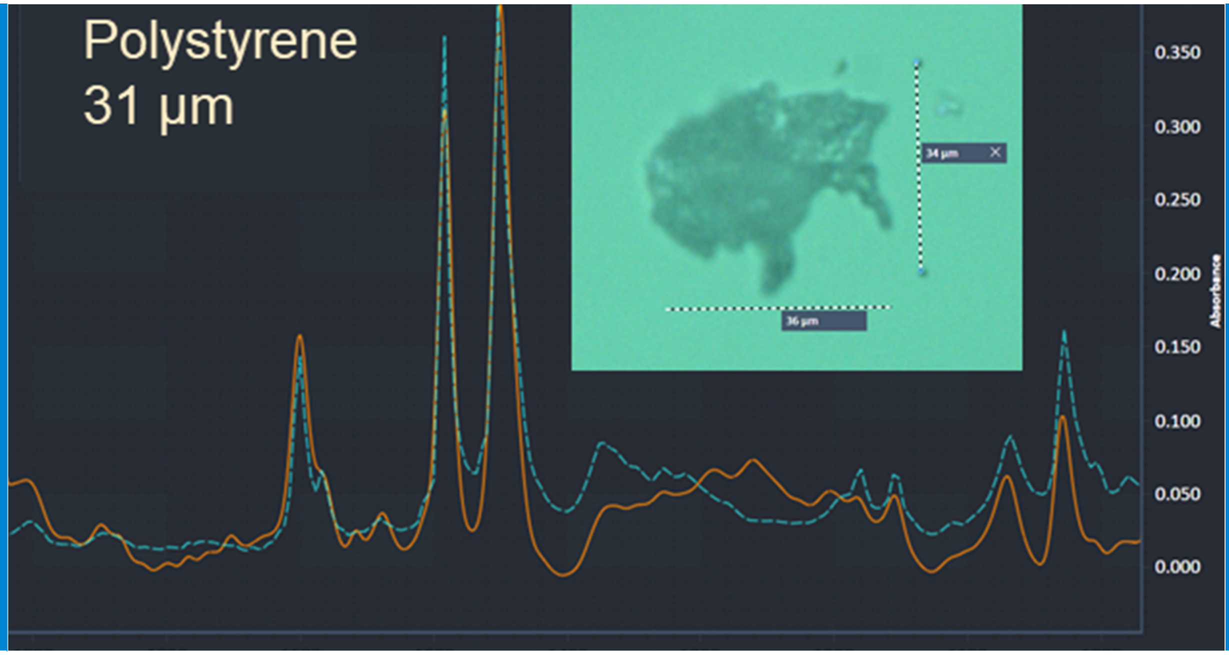


Analysis of Microplastics
A Challenge

Microplastics analysis require several different measurements depending on the goal and can include particle type, size, shape, area, & number

Hence there is no 'one' ideal solution for all the measurements but complementary techniques are required.





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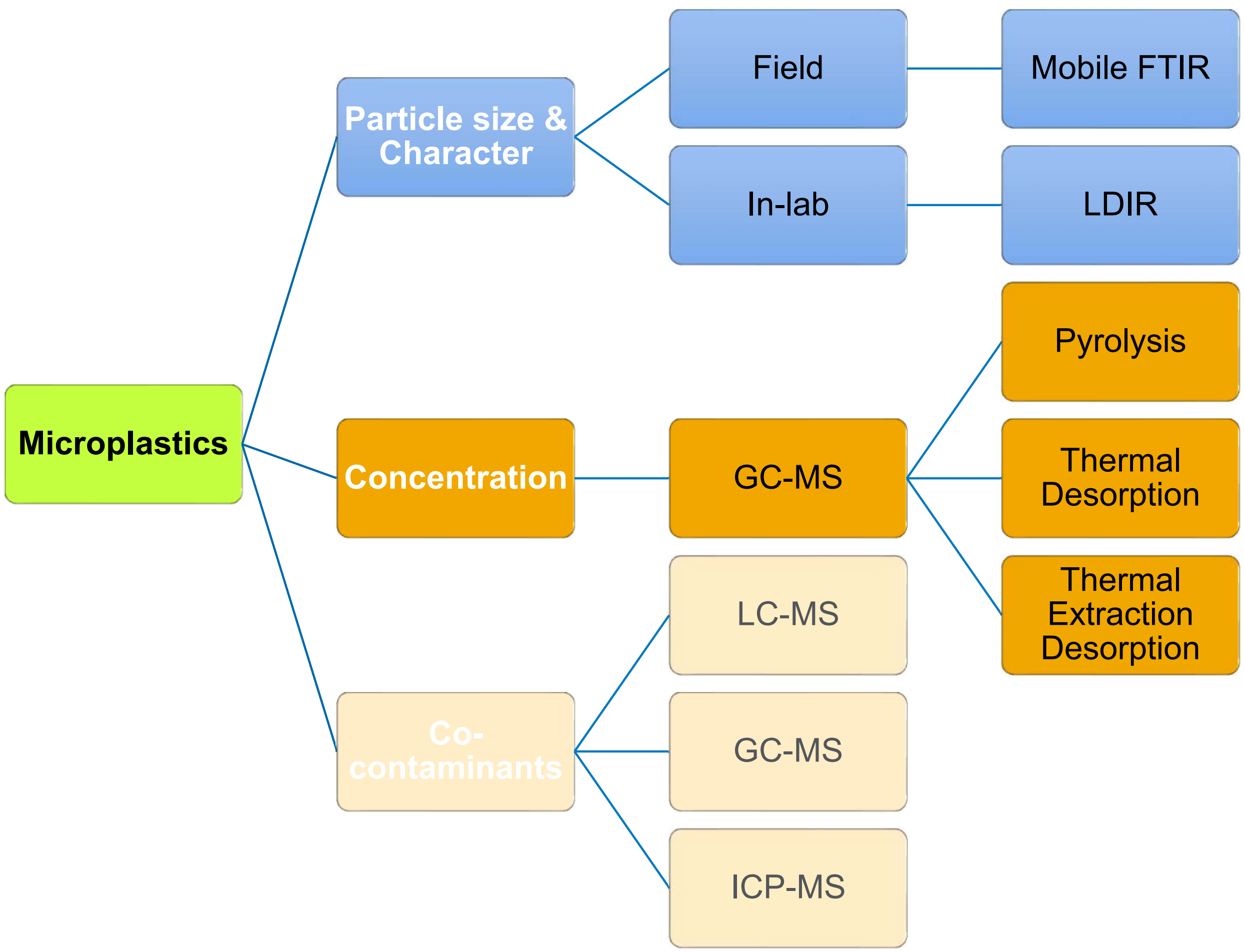
Analysis of Microplastics in the Environment
Measurement technique selected depends upon question(s) being asked

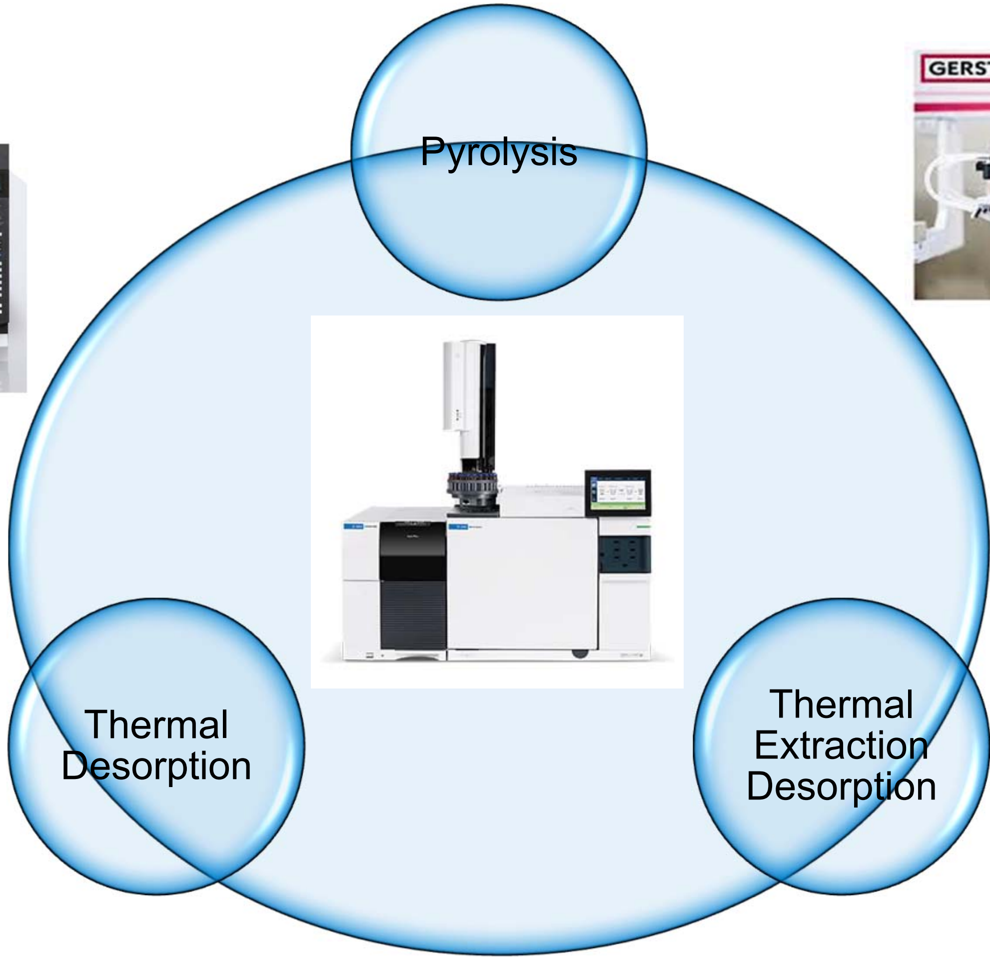
	Spectroscopic					Thermal	
	Optical/Fluorescence Microscopy	ATR-FTIR	µFT-IR Imaging/LDIR	NIR	µRaman	Pyr-GC/MS	T(E)D-GC/MS
Particle number	✓	✗	✓	✓	✓	✗	✗
ID	✗	✓	✓	✓	✓	✓*	✓*
Area/Shape	✓	✓	✓	✓	✓	✗	✗
Mass Fraction conc.	✗	✗	✗	✗	✗	✓	✓

* Some types of plastics

Microplastics Measurement



Sample introduction approaches for mass fraction Microplastics analysis



Thermogravimetric Analysis with Evolved Gas Analysis
Why Pyrolysis?

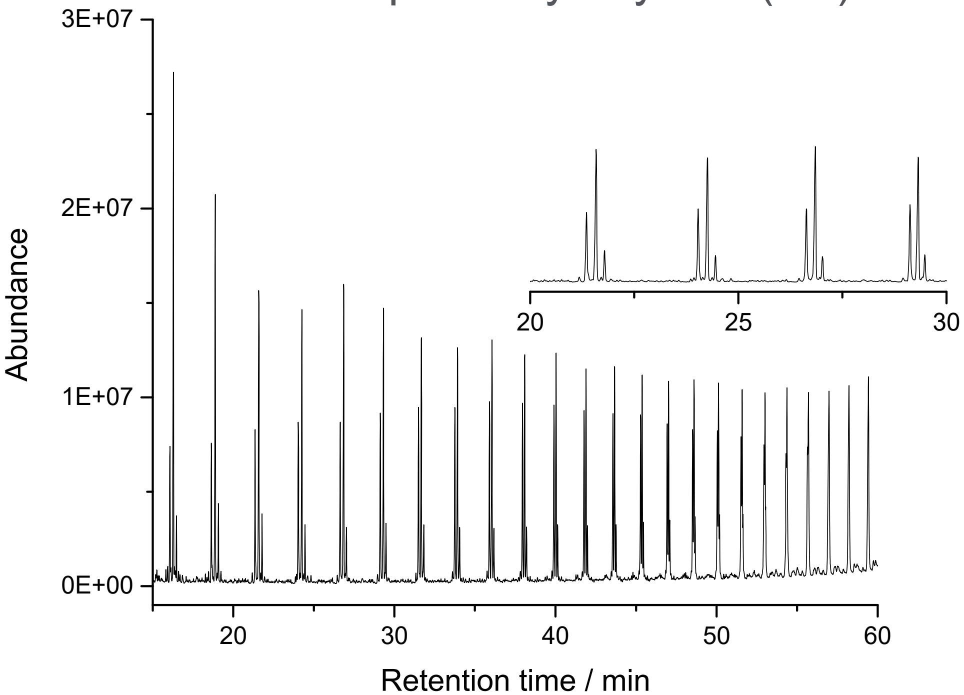
Decomposition temperature area of environmental matrices: 100 – 600°C

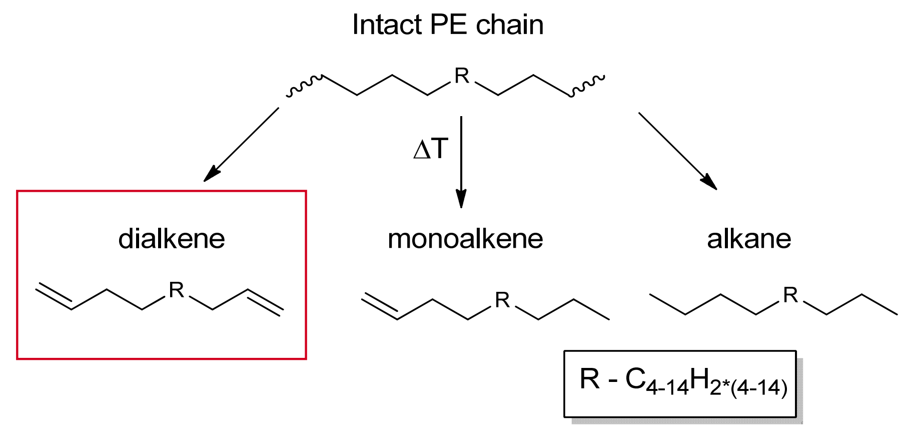
	PP	PE	PET	PS	PA6	PVC
Decomposition temperature area / °C	380 – 480	400 – 500	350 – 450	360 – 450	375 – 480	200 - 500
Gaseous decomposition products	methyl sub. alkanes + alkenes	alkenes, alkanes	CO_2, ethene, arylic acids, esters	styrene, styrene derivates, oligomers	CO_2, NH_3, capro-lactam, amides	HCl, methane, alkene

➡ Chromatographic separation of decomposition products is necessary

Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC-MS)

Example: Polyethylene (PE)





➡ Certain identification is possible, but only with small sample mass
(~ max. 1 mg or organic substances)

Pyrolysis GC/MS for Microplastics
Several Agilent users performing this analysis

Application Note
Environmental

Agilent
Trusted Answers

Quantification of Microplastics in Environmental Samples Using Pyrolysis and GC/MSD

Authors

George Dierkes,
Susanne Becher,
Heike Schumacher, and
Corinna Földi
German Federal Institute of Hydrology, Koblenz, Germany

Tim Lauschke, and
Thomas Ternes
Institute of Integrated Natural Sciences, University Koblenz-Landau, Germany

Joerg Riener
Agilent Technologies, Inc.

Abstract

There is growing interest in quantifying microplastics in environmental samples. This application note presents a robust pressurized liquid extraction (PLE) with pyrolysis-gas chromatography-mass spectrometry (pyr-GC/MS) method for quantitation of microplastics like polyethylene (PE), polypropylene (PP), and polystyrene (PS) at low concentrations in environmental matrices using the Agilent 5977B GC/MSD, Agilent 7890B GC, and Agilent MassHunter workstation software. Linearity, limits of quantitation (LOQs), and reproducibility for real environmental samples were evaluated. The GC/MSD addressed the insufficient limits of detection that have challenged previous methods. PE, PP, and PS microplastics were quantified down to 0.005 mg/g. Excellent linearity (R^2 >0.97) for calibration samples from 0.005 to 1 mg/g was obtained. Relative standard deviations (RSDs) for both spiked and environmental samples were <10% or lower, demonstrating excellent system reproducibility and reliability.

Agilent Application: 5994-2199EN

Analytical and Bioanalytical Chemistry (2019) 411:6959–6968
https://doi.org/10.1007/s00216-019-02066-9

RESEARCH PAPER

Check for updates

Quantification of microplastics in environmental samples via pressurized liquid extraction and pyrolysis-gas chromatography

Georg Dierkes[1] · Tim Lauschke[1,2] · Susanne Becher[1] · Heike Schumacher[1] · Corinna Földi[1] · Thomas Ternes[1,2]

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Environmental Science & Technology
Article
pubs.acs.org/est

Simultaneous Trace Identification and Quantification of Common Types of Microplastics in Environmental Samples by Pyrolysis-Gas Chromatography–Mass Spectrometry

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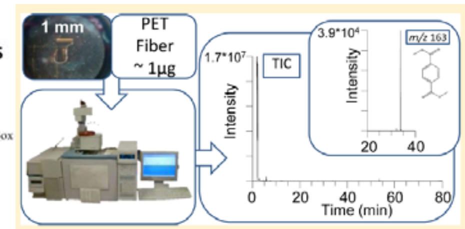
Institute for Chemistry and Biology of the Marine Environment (ICBM), Carl von Ossietzky University of Oldenburg, P.O. Box 2503, D-26111 Oldenburg, Germany



PE, PP, PS, PVC, PET, PC, PMMA, PA6

analytical chemistry
Technical Note
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Cloud-Point Extraction Combined with Thermal Degradation for Nanoplastic Analysis Using Pyrolysis Gas Chromatography–Mass Spectrometry

Xiao-xia Zhou,[†,‡] Li-teng Hao,[‡] Huang-ying-zi Wang,[†] Ying-jie Li,[‡] and Jing-fu Liu*,[‡]

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Thermal Extraction-Desorption Gas Chromatography Mass Spectrometry. TED-GC/MS

Components of TED-GC/MS

- Agilent 8890 GC
- Agilent 5977B GC/MSD
- Gerstel TDU
- Gerstel Twister
- Metller Toledo TGA

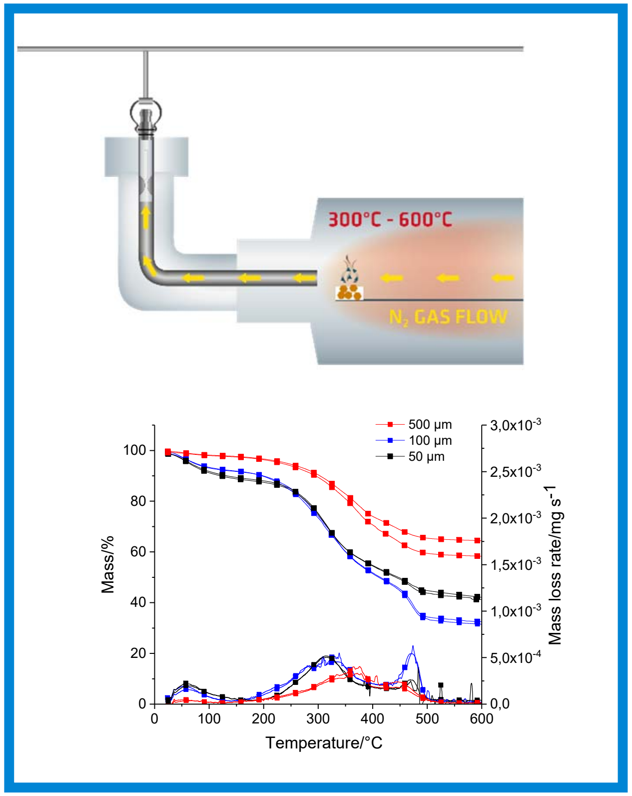
Advantages:

Fully automated including sample prep.
Homogeneity control with TGA
Better sample cleanup
Higher sample loads
More sensitivity

TED-GC-MS:
1st Part: Thermoextraction

Environmental sample = matrix + microplastics

Thermobalance



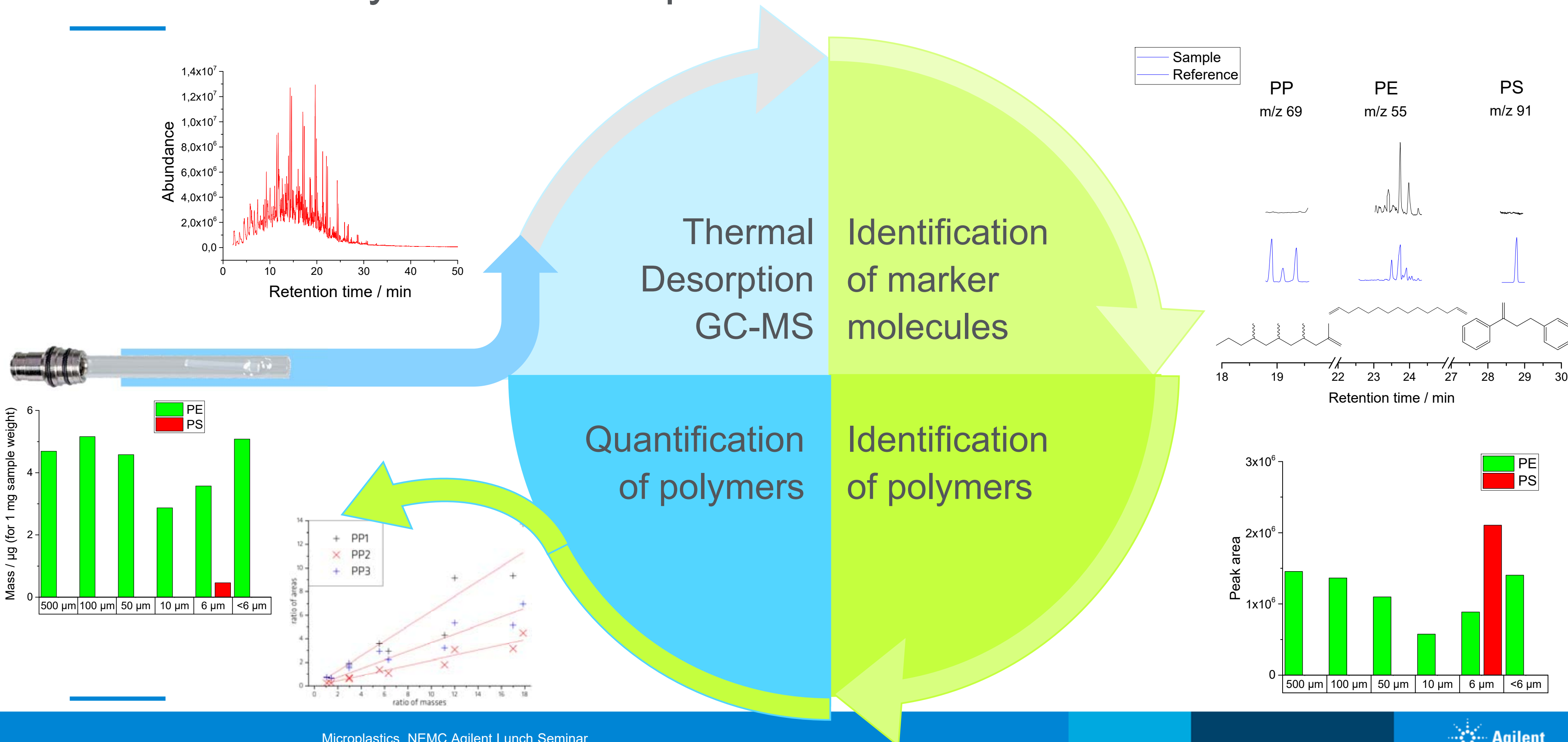
Adsorber loaded with decomposition products

Pyrolysis: inert atmosphere

RT – 600 °C: Pyrolytic decomposable organic compounds

TGA signal: Homogeneity control

TED-GC-MS
2nd Part: Analysis of Decomposition Products



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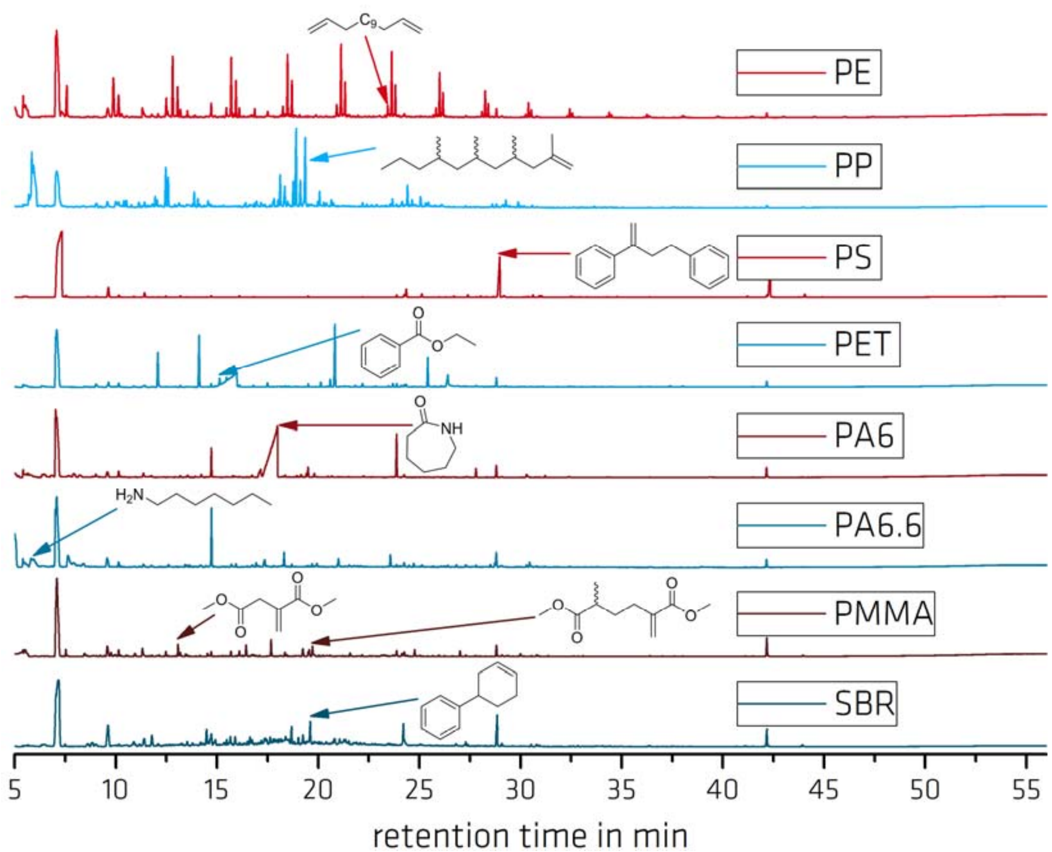
TED-GC-MS
specific decomposition products of polymers

- PE, PP, PS
- PET, PA, PMMA
- PBAT, PLA
- SBR = Styrene-Butadiene-Rubber (component of tyres)

- LOD: between 0.08 µg (PS) and 2.2 µg (PE)



Thermal Extraction Desorption-Gas chromatography-Mass Spectrometry (TED-GC-MS)

Water Research 85 (2015) 451–457
Contents lists available at ScienceDirect
Water Research
journal homepage: www.elsevier.com/locate/watres

Analysis of polyethylene microplastics in environmental samples, using a thermal decomposition method

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[b] UBA Umweltbundesamt, Wörlitzer Platz 1, 06844 Dessau-Roßlau, German
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journal homepage: www.elsevier.com/locate/envpol

Comparison of different methods for MP detection: What can we learn from them, and why asking the right question before measurements matters?☆

Anna M. Elert*, Roland Becker, Erik Duemichen, Paul Eisentraut, Jana Falkenhagen, Heinz Sturm, Ulrike Braun
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- Literature

May. 29, 2018 SCIENCE CHEMISTRY & PHYSICS

Polymer Analysis and Microplastics in the Environment

TED-GC-MS, a New and Fast Method

Read article as PDF

G.I.T. LABORATORY JOURNAL

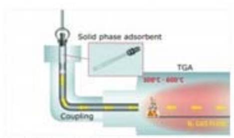

Fig. 1: Schematic of the thermal extraction (pyrolytic decomposition) of a sample in the TGA and transport of the resulting decomposition fragments to a solid-phase adsorbent, which is positioned in a thermal desorption glass tube located in a newly developed coupling device.

The abbreviation TED-GC-MS describes a two-step method for volatile diagnostics

Journal of Chromatography A, 1592 (2019) 133–142
Contents lists available at ScienceDirect
Journal of Chromatography A
journal homepage: www.elsevier.com/locate/chroma

Automated thermal extraction-desorption gas chromatography mass spectrometry: A multifunctional tool for comprehensive characterization of polymers and their degradation products

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ABSTRACT

The TED-GC–MS analysis is a two-step method. A sample is first decomposed in a thermogravimetric analyzer (TGA) and the gaseous decomposition products are then trapped on a solid-phase adsorber. Subsequently, the solid-phase adsorber is analyzed with thermal desorption gas chromatography mass

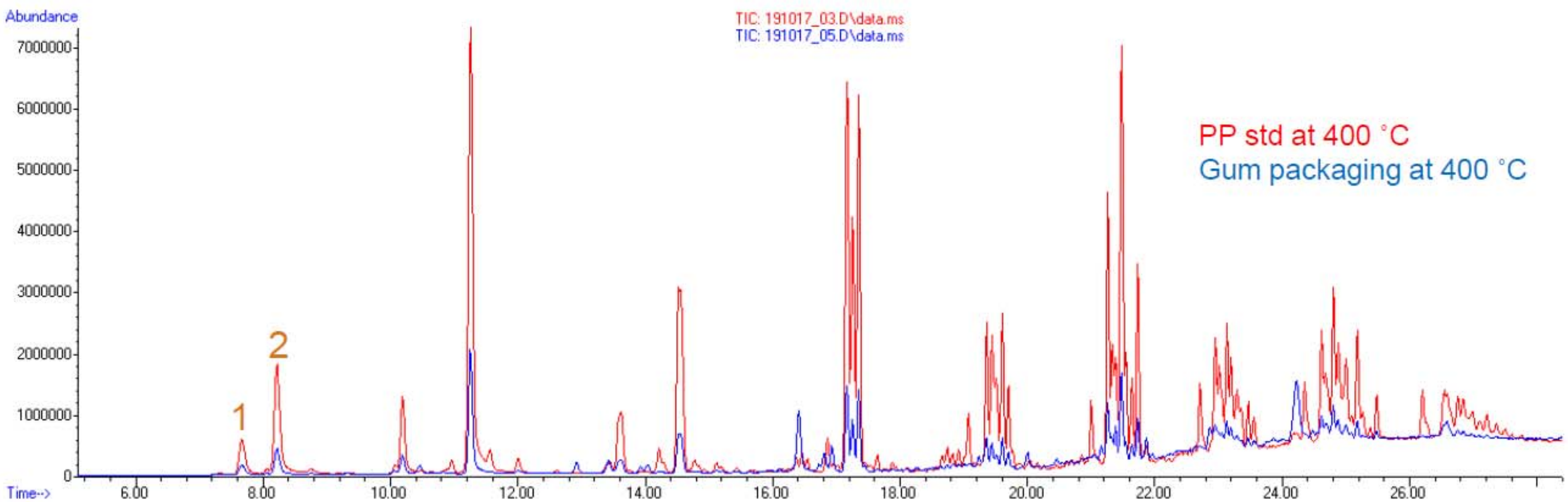
Unique markers via TD

Slide Courtesy: Markes Intl.
"Sampling & Analysis of Emerging Pollutants", Hannah Calder

Polypropylene (PP) real plastics, the whole profile

- PP std
- Gum packaging

- Unique Compounds:
  1. tert-butanol (7.7 min, 59 ion),
  2. 2-methyl pentane (8 min, 43/57/71 ions)



LC/MS/MS for specific plastics analysis

Environmental Science & Technology LETTERS

Letter

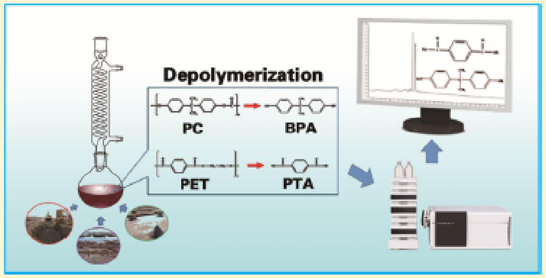
pubs.acs.org/journal/estlcu

A Simple Method for Quantifying Polycarbonate and Polyethylene Terephthalate Microplastics in Environmental Samples by Liquid Chromatography–Tandem Mass Spectrometry

Lei Wang,* Junjie Zhang, Shaogang Hou, and Hongwen Sun

Ministry of Education Key Laboratory of Pollution Processes and Environmental Criteria, Tianjin Key Laboratory of Environmental Remediation and Pollution Control, College of Environmental Science and Engineering, Nankai University, Tianjin 300350, China

Supporting Information



ABSTRACT: Microplastics (MPs) have frequently been found in the environment. However, studies of the quantification methods for MPs are still needed. Plastics are polymers with different degrees of polymerization. In this study, alkali-assisted thermal hydrolysis was applied to depolymerize two plastics containing ester groups, polycarbonate (PC) and polyethylene terephthalate (PET), in a pentanol or butanol system. By determining the concentrations of the depolymerized building block compounds, i.e., bisphenol A and *p*-phthalic acid, we quantified the amounts of PC and PET MPs in environmental samples. Recoveries of 87.2–97.1% were obtained for the PC and PET plastic particles spiked in the landfill sludge. The method was successfully applied to determine the occurrence of PC and PET MPs in samples of sludge, marine sediments, indoor dust, digestive residues in mussel and clam, and sea salt and rock salt. High concentrations of 246 and 430 mg/kg were determined for PC and PET type MPs, respectively, in an indoor dust. In addition, concentrations of 63.7 mg/kg for PC and 127 mg/kg for PET were detected in the digestive residues of a clam.

Analysis of emerging contaminants sorbed to Microplastics

Environmental Science & Technology
ACS AuthorChoice
Article
pubs.acs.org/est

Chemical Pollutants Sorbed to Ingested Microbeads from Personal Care Products Accumulate in Fish

Peter Wardrop,[†] Jeff Shimeta,[†] Dayanthi Nugegoda,[†] Paul D. Morrison,[†] Ana Miranda,[†] Min Tang,[‡] and Bradley O. Clarke*,[†]

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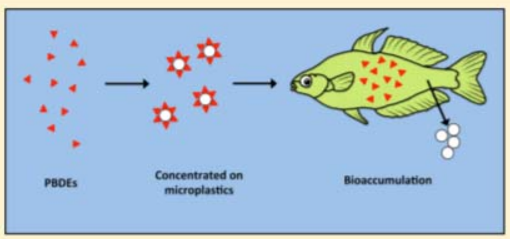
Supporting Information



ABSTRACT: The prevalence of microplastics (<5 mm) in natural environments has become a widely recognized global problem. Microplastics have been shown to sorb chemical pollutants from their surrounding environment, thus raising concern as to their role in the movement of these pollutants through the food chain. This experiment investigated whether organic pollutants sorbed to microbeads (MBs) from personal care products were assimilated by fish following particle ingestion. Rainbow fish (*Melanotaenia fluviatilis*) were exposed to MBs with sorbed polybrominated diphenyl ethers (PBDEs; BDE-28, -47, -100, -99, -153, -154, -183, 200 ng g^{-1}; BDE-209, 2000 ng g^{-1}) and sampled at 0, 21, 42, and 63 days along with two control treatments (food only and food + clean MBs). Exposed fish had significantly higher Σ_8PBDE concentrations than both control treatments after just 21 days, and continued exposure resulted in increased accumulation of the pollutants over the experiment (ca. 115 pg g^{-1} ww d^{-1}). Lower brominated congeners showed the highest assimilation whereas higher brominated congeners did not appear to transfer, indicating they may be too strongly sorbed to the plastic or unable to be assimilated by the fish due to large molecular size or other factors. Seemingly against this trend, however, BDE-99 did not appear to bioaccumulate in the fish, which may be due to partitioning from the MBs or it being metabolized in vivo. This work provides evidence that MBs from personal care products are capable of transferring sorbed pollutants to fish that ingest them.

Bradley Clarke
Melbourne University

7000 Series GC/TQ

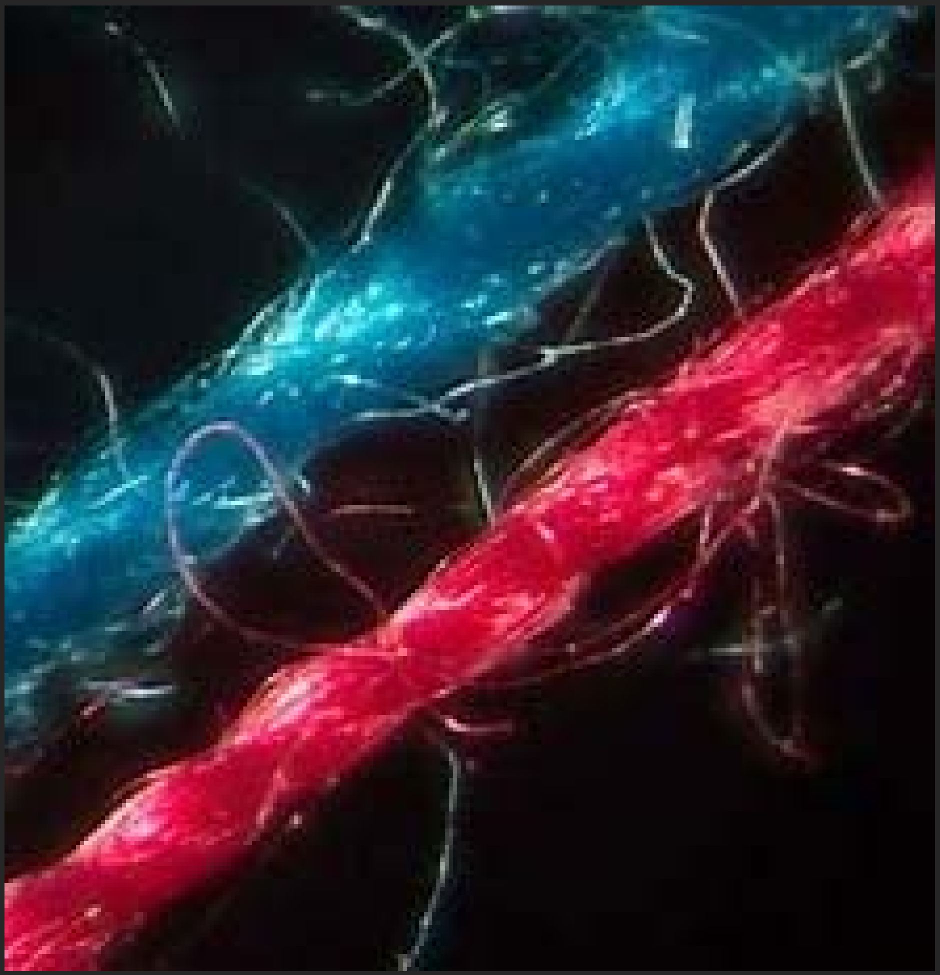
https://doi.org/10.1021/acs.est.5b06280

Microplastics Analysis:

Simplified Workflows for Comprehensive Characterization in the Environment

Jeff Prevatt, PhD

PIMA COUNTY
WASTEWATER RECLAMATION

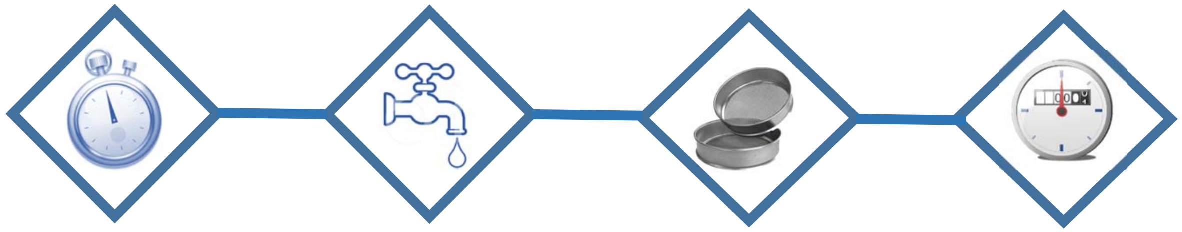




40
30
20
10
½mm

Workflow Development

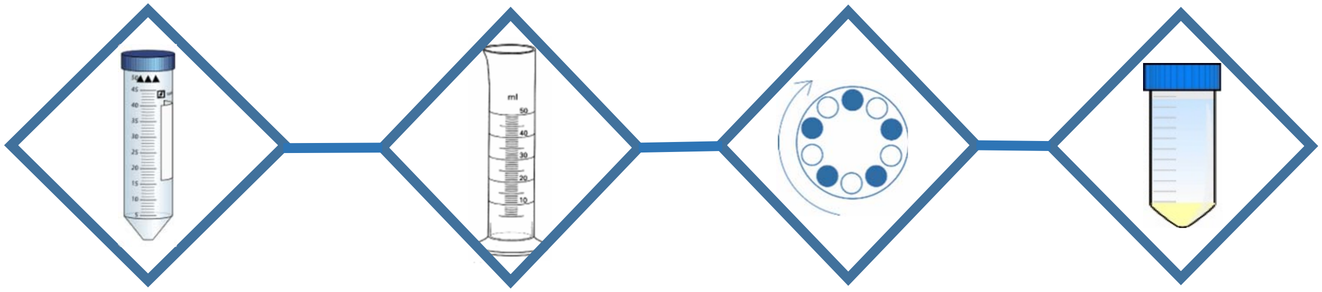
- Ease of use
- Sample preparation
- Speed of analysis
- Data interpretation
- Reporting

Sample Collection Workflow

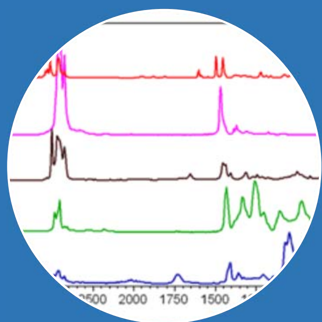


1. Straightforward
2. Simple to follow
3. Reproducible

Sample Preparation Workflow



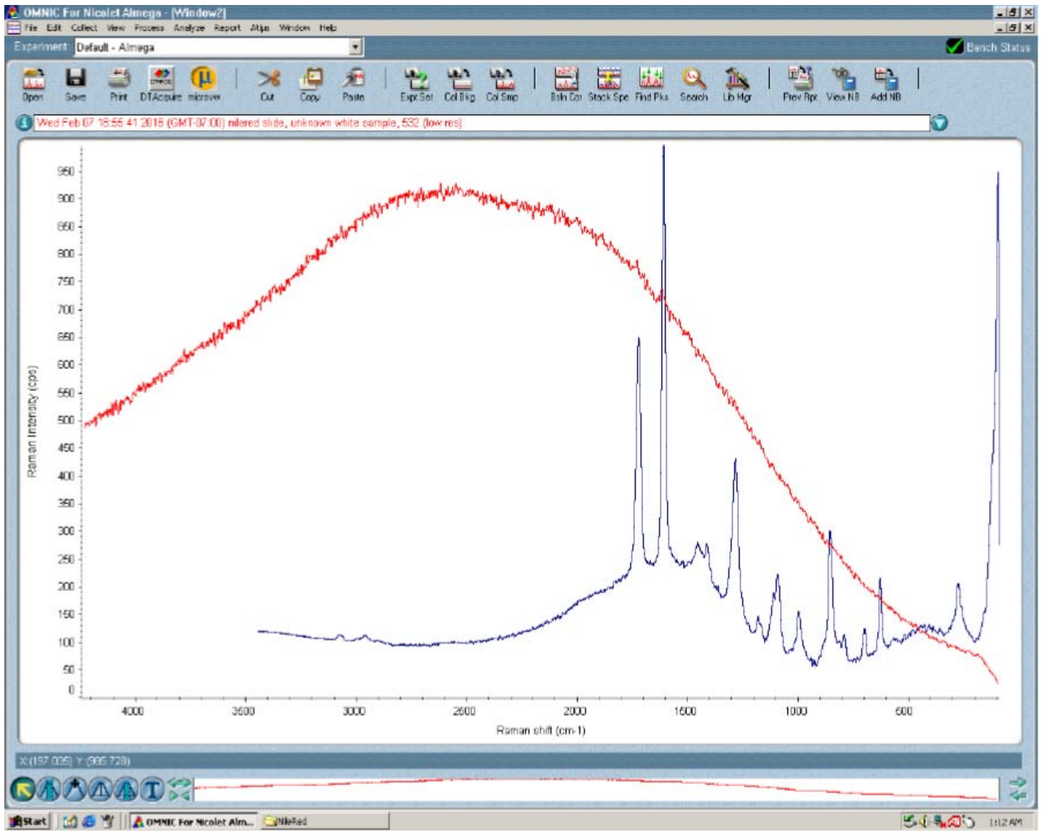
1. Easy to replicate
2. Addresses Interferences
3. Minimizes loss of particles



Sample Analysis Workflow

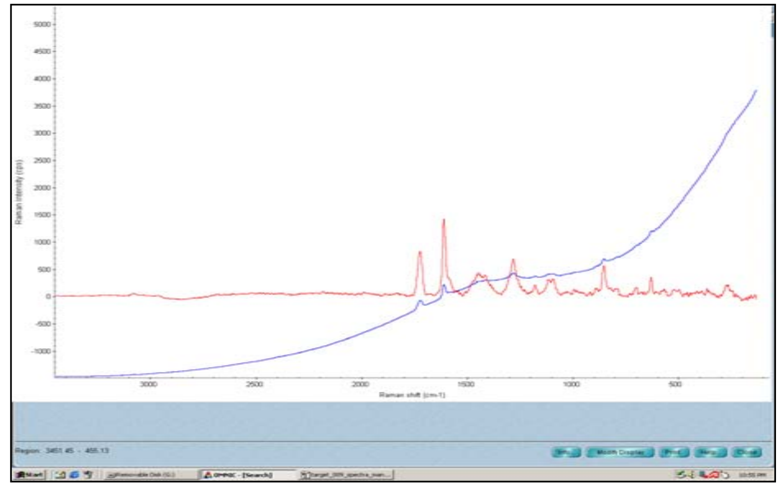
1. Identification of particles
2. Quantification of particles
3. Particle size distribution
4. Fast & reproducible

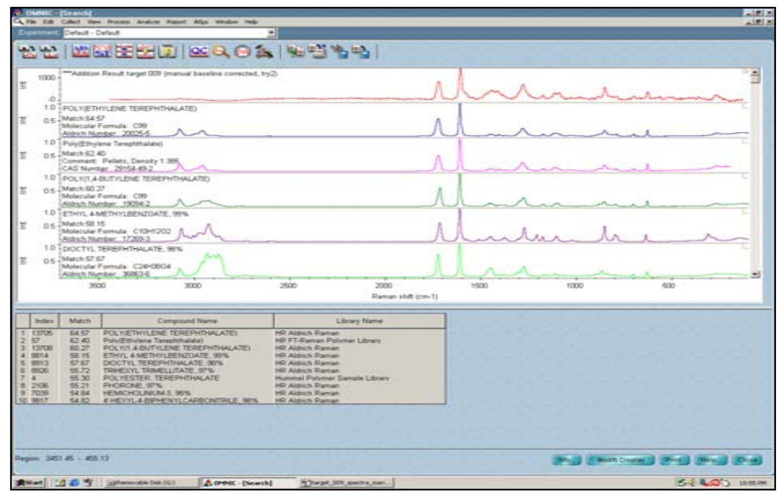
Micro-Raman Analysis



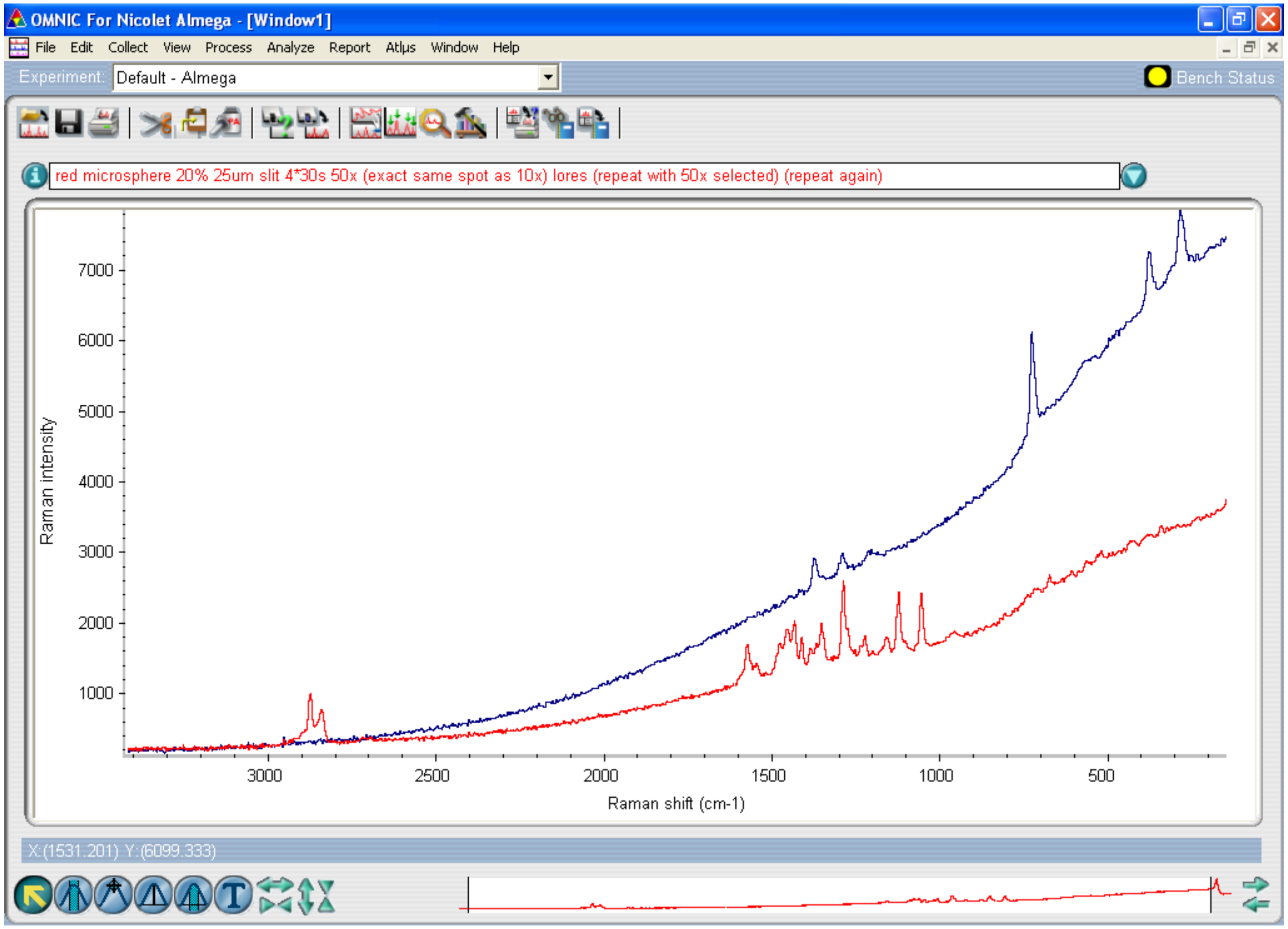
- ✓ FTIR and Raman spectroscopy are suitable for definitive identification of plastics
- ✗ 532 nm excitation source results in excessive fluorescence
- ✓ 785 nm excitation source produces acceptable signal for differentiating plastics

Polyethylene





Challenges



Instrument setting vary

Analysis times are slow

Multiple acquisitions required

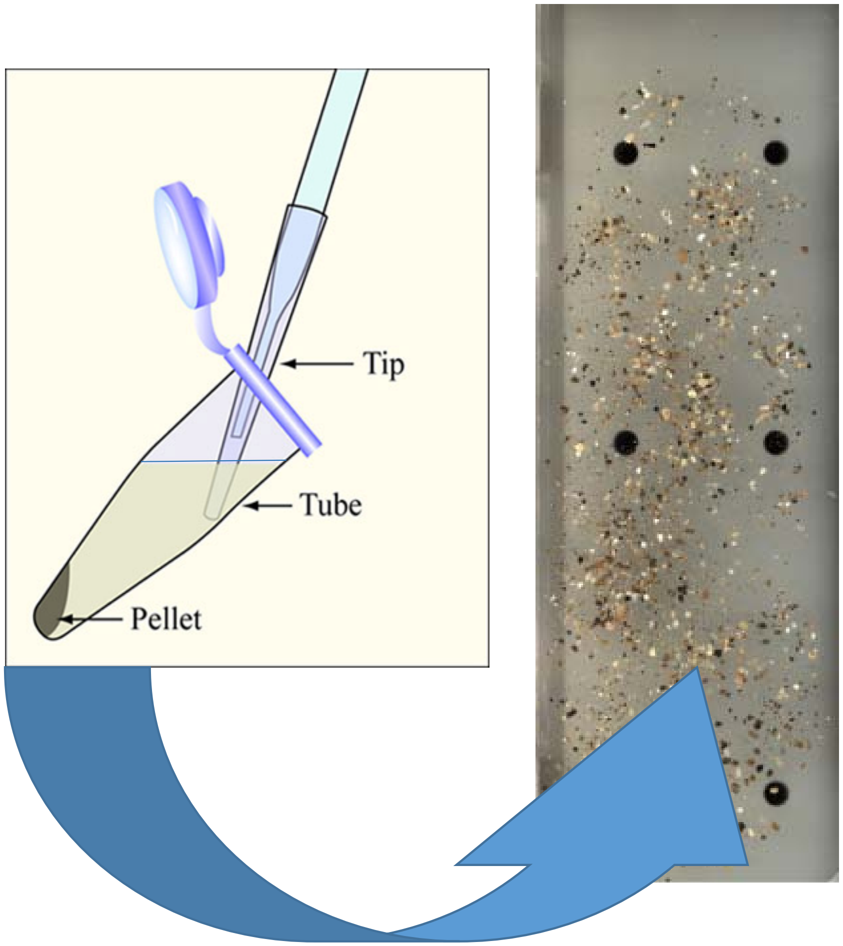
Samples easily damaged

Agilent LDIR 8700

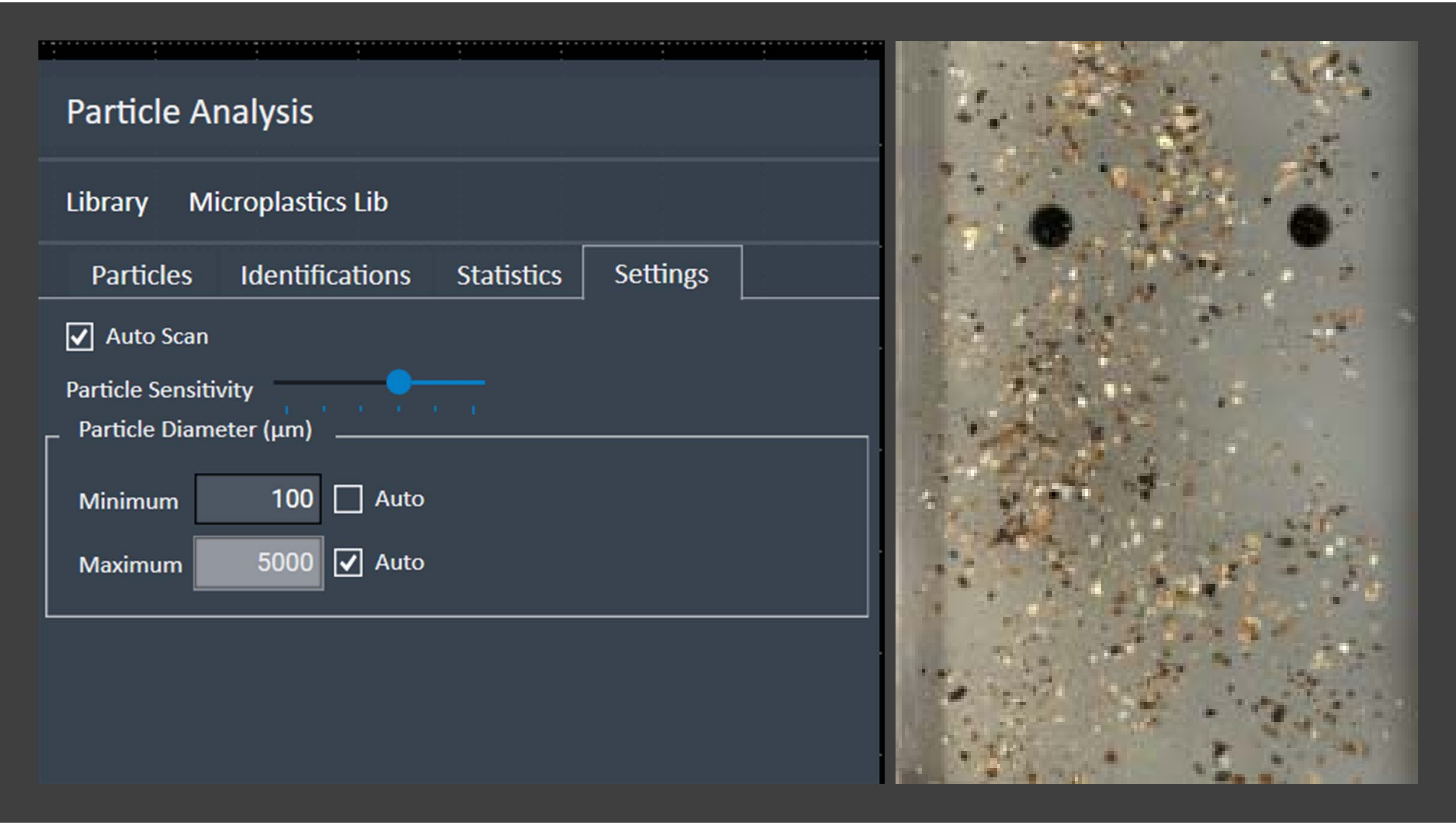
Chemical Imaging System

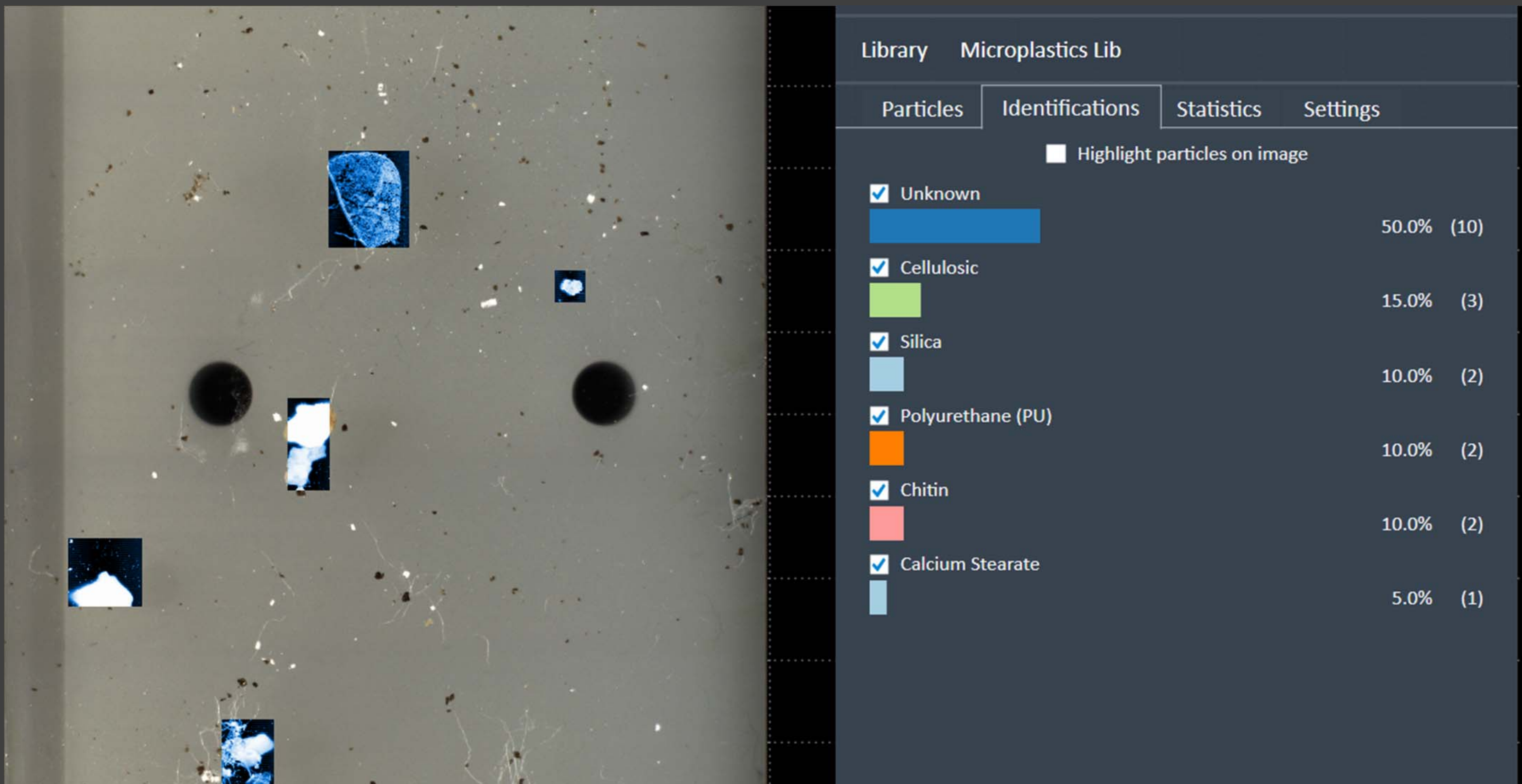
Agilent LDIR 8700

Specification	Description
Optical Resolution	1 micron
Spectral Resolution	20 micron
Wavelength Coverage	1,800 – 1,000 wavenumbers (cm^{-1})
Light Source	Quantum Cascade Laser
Detector	TE cooled MCT
Time Required for Analysis	Minutes to hours
Reference Library	IR reference and buildable

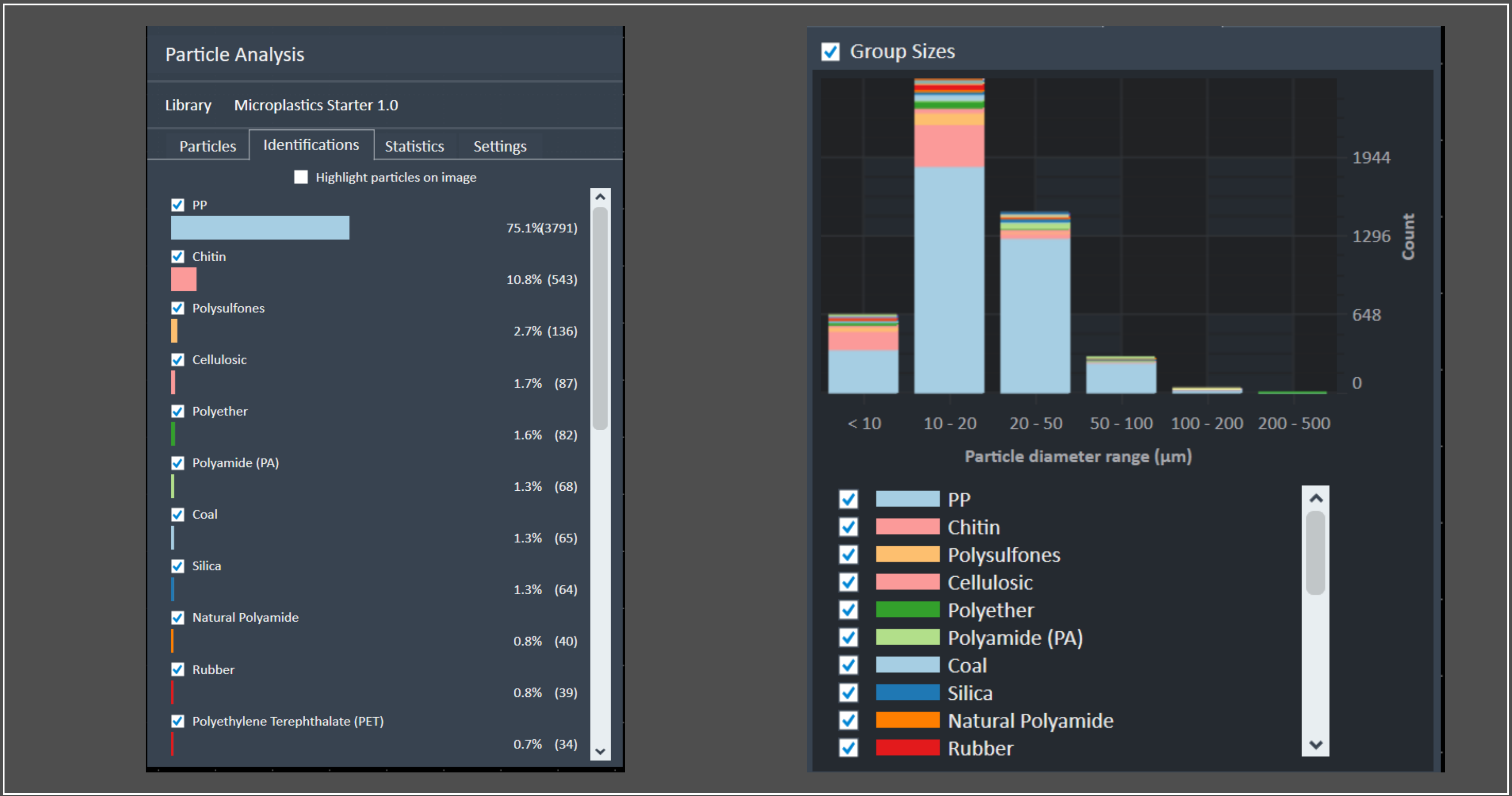


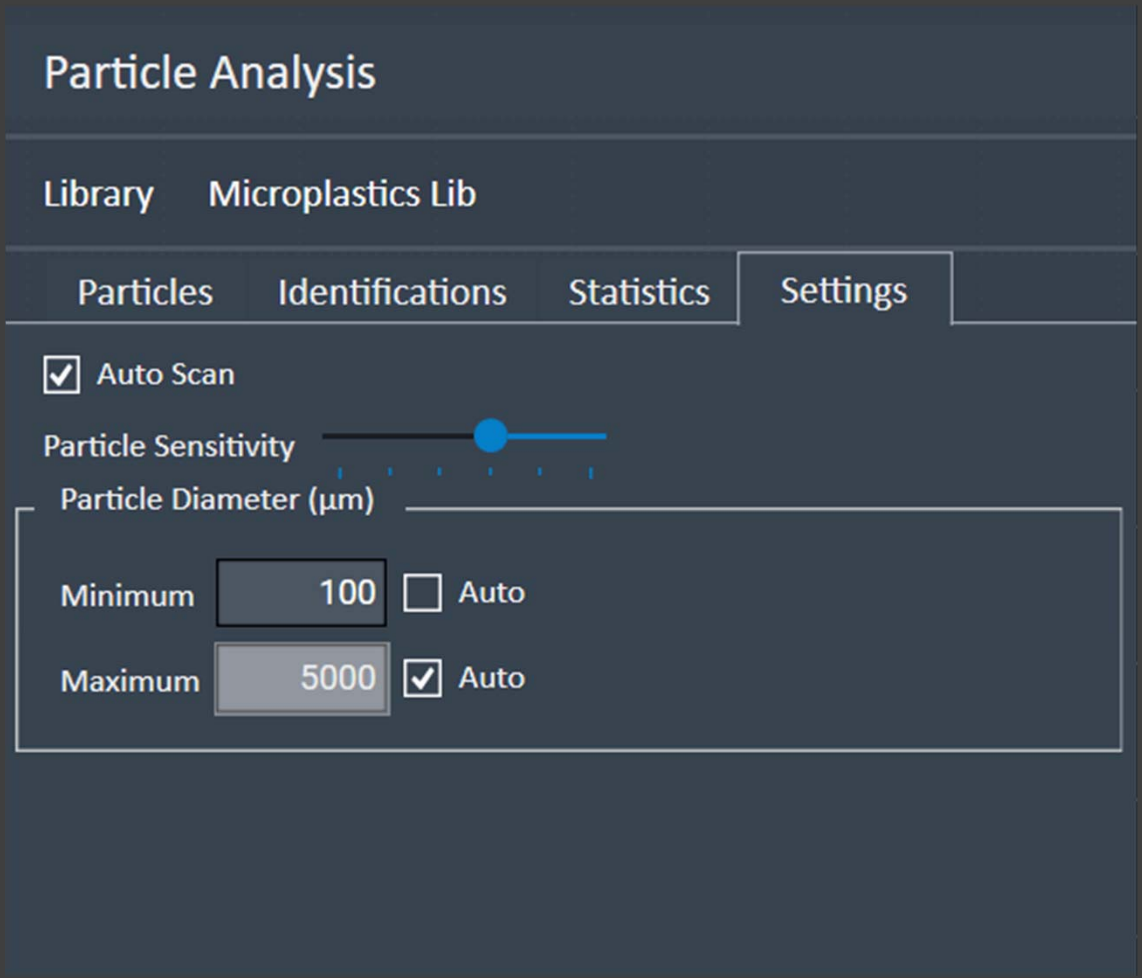
- Eliminates filtration and associated sample loss
- Cellulose removed
- Preparation time is ideal
- Sieved contents plated onto a slide
- Reference spike recovery near 100%

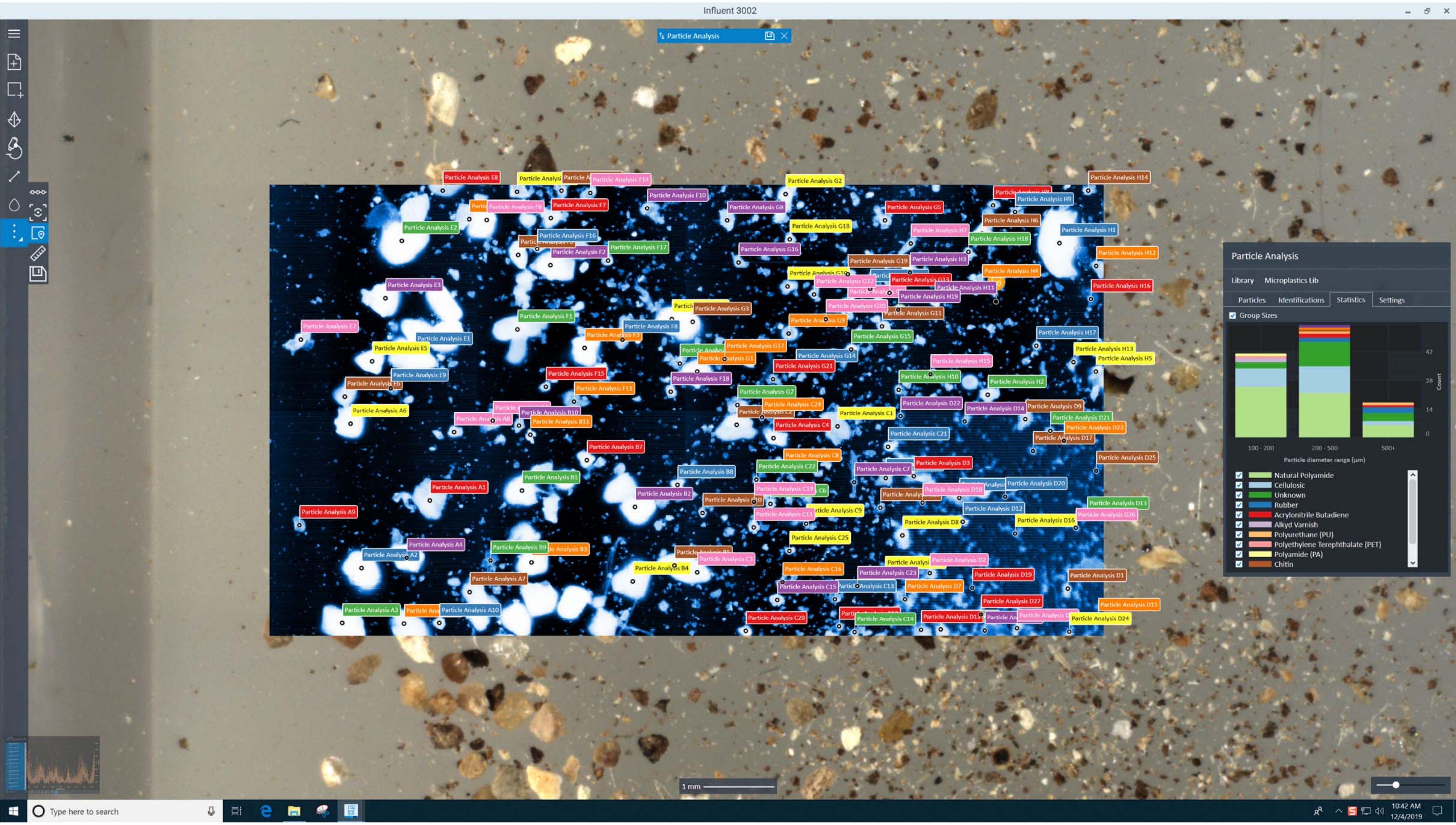

Particle Analysis
Library
Microplastics Lib
Particles
Identifications
Statistics
Settings
Auto Scan
Particle Sensitivity
Particle Diameter (µm)
Minimum
100
Auto
Maximum
5000
Auto



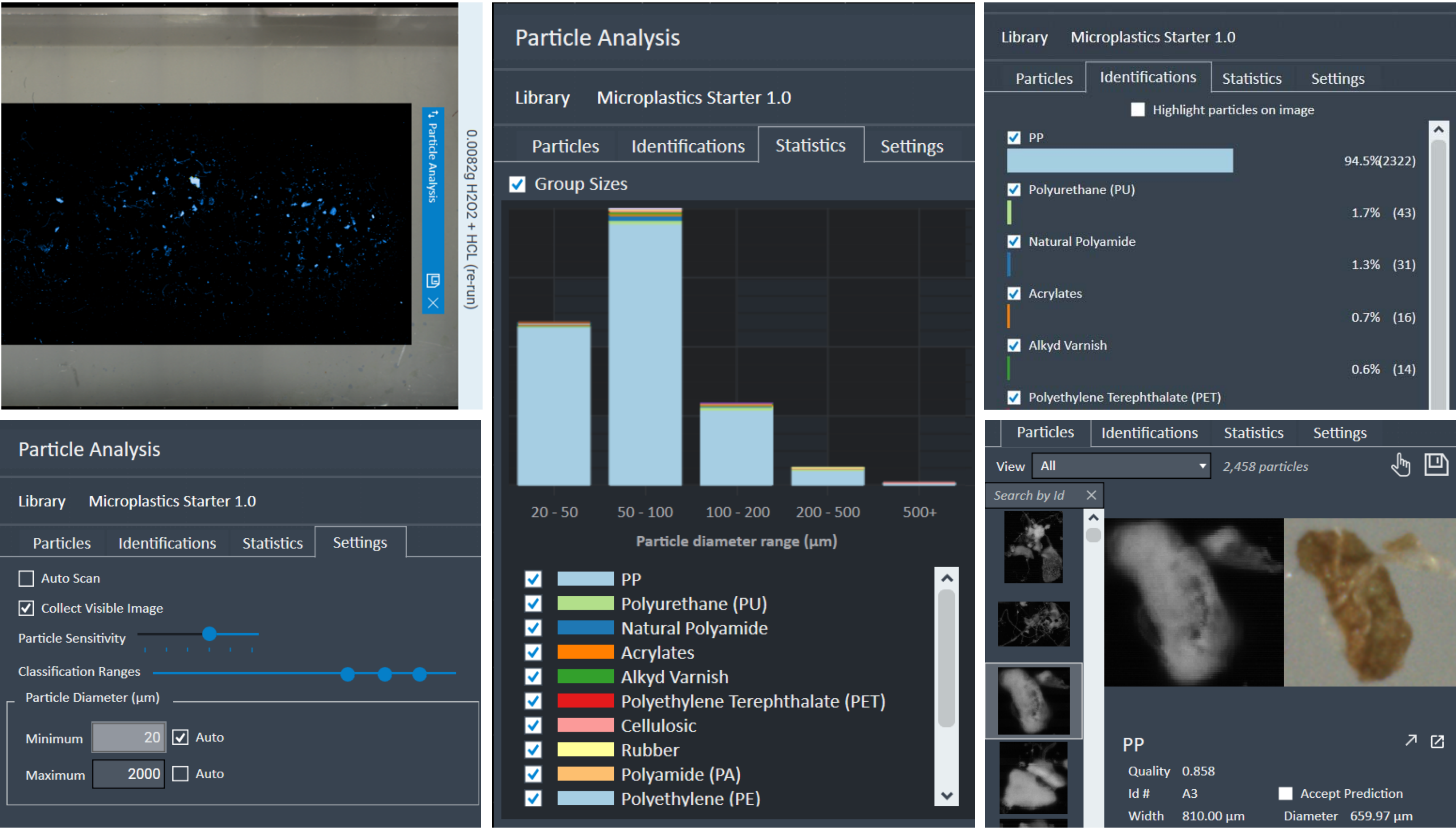
Library
Microplastics Lib
Particles
Identifications
Statistics
Settings
Highlight particles on image
Unknown
50.0% (10)
Cellulosic
15.0% (3)
Silica
10.0% (2)
Polyurethane (PU)
10.0% (2)
Chitin
10.0% (2)
Calcium Stearate
5.0% (1)


Particle Analysis
Library Microplastics Starter 1.0
Particles
Identifications
Statistics
Settings
Highlight particles on image
PP 75.1% (3791)
Chitin 10.8% (543)
Polysulfones 2.7% (136)
Cellulosic 1.7% (87)
Polyether 1.6% (82)
Polyamide (PA) 1.3% (68)
Coal 1.3% (65)
Silica 1.3% (64)
Natural Polyamide 0.8% (40)
Rubber 0.8% (39)
Polyethylene Terephthalate (PET) 0.7% (34)
Group Sizes
1944
1296
648
0
Count
< 10
10 - 20
20 - 50
50 - 100
100 - 200
200 - 500
Particle diameter range (µm)
PP
Chitin
Polysulfones
Cellulosic
Polyether
Polyamide (PA)
Coal
Silica
Natural Polyamide
Rubber


Particle Analysis
Library
Microplastics Lib
Particles
Identifications
Statistics
Settings
Auto Scan
Particle Sensitivity
Particle Diameter (µm)
Minimum
100
Auto
Maximum
5000
Auto



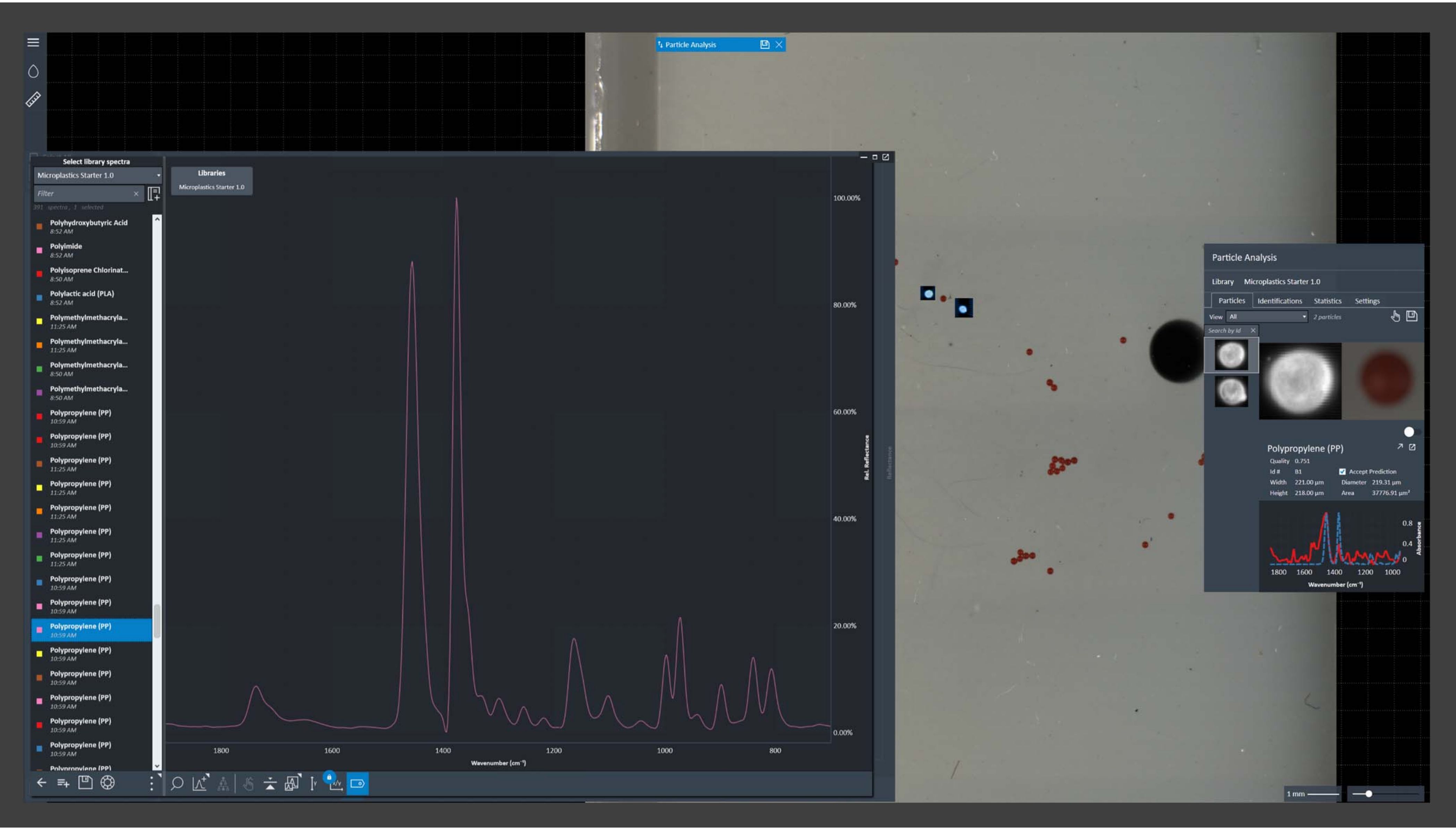
Influent 3002
Particle Analysis
Particle Analysis
Library
Microplastics Lib
Particles
Identifications
Statistics
Settings
Group Sizes
100 - 200
200 - 500
500+
Particle diameter range (µm)
Count
Natural Polyamide
Cellulosic
Unknown
Rubber
Acrylonitrile Butadiene
Alkyd Varnish
Polyurethane (PU)
Polyethylene Terephthalate (PET)
Polyamide (PA)
Chitin
1 mm
Type here to search
10:42 AM
12/4/2019



Particle Analysis
0.0082g H2O2 + HCL (re-run)
Particle Analysis
Library Microplastics Starter 1.0
Particles Identifications Statistics Settings
Group Sizes
20 - 50
50 - 100
100 - 200
200 - 500
500+
Particle diameter range (µm)
PP
Polyurethane (PU)
Natural Polyamide
Acrylates
Alkyd Varnish
Polyethylene Terephthalate (PET)
Cellulosic
Rubber
Polyamide (PA)
Polyethylene (PE)
Library Microplastics Starter 1.0
Particles Identifications Statistics Settings
Highlight particles on image
PP 94.5% (2322)
Polyurethane (PU) 1.7% (43)
Natural Polyamide 1.3% (31)
Acrylates 0.7% (16)
Alkyd Varnish 0.6% (14)
Polyethylene Terephthalate (PET)
Particle Analysis
Library Microplastics Starter 1.0
Particles Identifications Statistics Settings
Auto Scan
Collect Visible Image
Particle Sensitivity
Classification Ranges
Particle Diameter (µm)
Minimum 20 Auto
Maximum 2000 Auto
Particles Identifications Statistics Settings
View All 2,458 particles
Search by Id
PP
Quality 0.858
Id # A3
Accept Prediction
Width 810.00 µm
Diameter 659.97 µm

Reproducibility

Sample Analyzed	LDIR Particle Count	Usable Partiles Identified	Acrylonitrile Butadiene	Alkyd Varnish	Calcium Stearate	Cellulosic	Chitin	Coal	Natural Polyamide	Polyamide (PA)	Polyethylene (PE)	Polyethylene Terephthalate (PET)	Polyimide	Polypropylene (PP)	Polytetrafluoroethylene (PTFE)	Polyurethane (PU)	Rubber	Silica
Run 1	136	132	7	5	4	12	1	0	60	9	2	2	0	9	1	19	1	0
Run 2	138	131	3	1	5	12	1	1	63	7	2	1	0	9	1	25	0	0
Run 3	136	131	7	3	5	12	0	0	65	10	2	1	0	8	0	16	2	1
Run 4	140	135	7	6	5	12	0	1	63	11	2	1	1	8	1	17	0	0
Run 5	136	127	8	4	6	7	2	2	60	10	2	1	1	8	0	12	3	1
Run 6	137	130	1	1	5	12	1	2	60	11	2	2	0	8	0	24	1	0
Run 7	137	127	0	2	6	13	1	1	58	9	2	1	0	8	0	26	0	0
Run 8	135	135	0	3	6	11	1	3	58	9	1	0	1	9	1	25	1	0
True Number:														10				
Mean Detected:	137	131	4.13	3.13	5.25	11.4	0.88	1.25	60.9	9.5	1.88	1.13	0.38	8.38	0.5	20.5	1	0.25
Percent Recovery:														83.8				
Std Dev:	1.55	3.07	3.48	1.81	0.71	1.85	0.64	1.04	2.53	1.31	0.35	0.64	0.52	0.52	0.53	5.21	1.07	0.46
Relative Std Dev:	1.13	2.34	84.4	57.8	13.5	16.2	73.2	82.8	4.16	13.8	18.9	57	138	6.18	107	25.4	107	185


Particle Analysis
Select library spectra
Microplastics Starter 1.0
Filter
Libraries
Microplastics Starter 1.0
Polyhydroxybutyric Acid
Polyimide
Polyisoprene Chlorinat...
Polylactic acid (PLA)
Polymethylmethacryla...
Polypropylene (PP)
100.00%
80.00%
60.00%
40.00%
20.00%
0.00%
Rel. Reflectance
1800
1600
1400
1200
1000
800
Wavenumber (cm⁻¹)
Particle Analysis
Library Microplastics Starter 1.0
Particles Identifications Statistics Settings
View All
2 particles
Search by id
Polypropylene (PP)
Quality 0.751
Id # 81
Accept Prediction
Width 221.00 µm
Diameter 219.31 µm
Height 218.00 µm
Area 37776.91 µm²
Absorbance
Wavenumber (cm⁻¹)
1 mm


Thank You!
Sidorovstock/AdobeStock